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Isotopic evidence for biogenic molecular hydrogen production in the Atlantic Ocean

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Supplement

Due to the experimental upset and timing the following assumption have been made:

- The glass vessel is initially under vacuum.
- The water sample flows into the glass vessel, equilibrates with the headspace and mix completely with the injected makeup gas.
- No significant exchange between the headspace / makeup gas mixture and the water phase will happen until the sample has been extracted into an evacuated flask.

The following abbreviations and definitions have been used:

- V_h: volume headspace in the glass vessel (1.6 dm^3)
- V_w: volume water in the glass vessel (8.4 dm^3)
- V_t: volume gas transfer system (0.025 dm^3)
- V_f: volume flask and drying tube (1.1 dm^3)
- p_h: pressure headspace after transfer from Niskin bottle to glass vessel
- p_{ht}: pressure headspace and gas transfer system before addition of makeup gas
- p_{htm}: pressure headspace and gas transfer system after addition of makeup gas
- p_f: pressure headspace, gas transfer system and flask after expansion to flask
- c_{w0}: initial H_2 concentration in seawater
- c_h: H_2 concentration in headspace after transfer from Niskin bottle to glass vessel
- c_w: H_2 concentration in seawater after transfer from Niskin bottle to glass vessel
- y_h: H_2 wet mole fraction in headspace after transfer from Niskin bottle to glass vessel
- y_m: H_2 dry mole fraction makeup gas
- y_{htm}: H_2 wet mole fraction in headspace and gas transfer system after addition of makeup gas
- y_f: H_2 dry mole fraction sample flask
- R: ideal gas constant (= 8.31446621 J K^{-1} mol^{-1})
- T: ambient absolute temperature (assumed to be equal to the gas temperature)

Defining the **extraction efficiency η** as

$$\eta = \frac{c_h V_h}{c_{w0} V_w} \tag{1}$$

the **initial concentration of H_2 in seawater, c_{w0},** can be calculated from

$$c_{w0} = \frac{c_h V_h}{\eta V_w} \tag{2}$$

The concentration in the headspace, c_h, was not measured directly, but can be derived from the measured H_2 mole fraction in the sampling flask. The sampling procedure following gas extraction under vacuum can be broken into three steps (see Methods section):

1. Expansion of headspace
2. Addition of makeup gas
3. Expansion of headspace/makeup gas mixture into sampling flask

Step 1: The volume of the headspace increases from V_h to $V_h + V_t$, where V_t is the volume of the gas transfer system. The total pressure drops from p_h to $p_{ht} = p_h\, V_h / (V_h + V_t)$. H_2 mole fraction, y_h, and isotope delta, δ_h, do not change.

Step 2: Adding makeup gas changes the total pressure from p_{ht} to p_{htm}. H_2 mole fraction and isotope delta also change. The H_2 mole fraction after mixing with makeup gas is:

$$y_{htm} = (y_h - y_m)\frac{p_{ht}}{p_{htm}} + y_m \tag{3}$$

The initial headspace H_2 concentration is calculated using the ideal gas law:

$$\begin{aligned} c_h &= \frac{y_h p_h}{RT} = \frac{p_h}{RT}\left[(y_{htm} - y_m)\frac{p_{htm}}{p_{ht}} + y_m\right] \\ &= \frac{1}{RT}\left[(y_{htm} - y_m)p_{htm}\left(1 + \frac{V_t}{V_h}\right) + y_m p_h\right] \end{aligned} \tag{4}$$

Step 3: The gas is expanded from the manifold into a sampling flask, passing through a drying trap. At this stage the mole fractions are changed due to drying of the gas. The volume of the system also changes, but this affects the H_2O and H_2 mole fractions by the same ratio.

Thus, y_{htm} is calculated from the measured dry mole fraction in the flask, y_f, as

$$y_{htm} = y_f\left[1 - \frac{p_h(H_2O)}{p_{htm}}\frac{V_h}{V_h + V_t}\right] \tag{5}$$

where $p_h(H_2O)$ is the initial water vapour pressure in the headspace. Due to the short time periods involved (< 4 min), water vapour equilibration is assumed not to occur upon subsequent pressure changes in the system.

Combining equations (2), (4) and (5), the initial seawater concentration can be calculated as

$$\begin{aligned} c_{w0} &= \frac{(y_{htm} - y_m)(V_h + V_t)p_{htm} + y_m V_h p_h}{\eta V_w RT} \\ &= \frac{y_f\left[\left(1 + \frac{V_t}{V_h}\right)p_{htm} - p_h(H_2O)\right] - y_m\left[\left(1 + \frac{V_t}{V_h}\right)p_{htm} - p_h\right]}{\eta V_w RT} \end{aligned} \tag{6}$$

y_f, y_m, p_{htm}, V_t, V_h and V_w were measured. R is a constant (= 8.31446621 J K^{-1} mol^{-1}).

T is the ambient lab temperature and assumed to be equal to the gas and water temperature. Since ambient lab temperature and surface water temperature were never more than 1.2 ºC apart, this assumption is unlikely to cause and error of more than 0.4 % in c_{w0}.

$p_h(H_2O)$ was assumed to be equal to the equilibrium vapour pressure (calculated following Green and Carritt (1967)) of seawater at temperature T and at its actual salinity, which was measured to within 0.01 g kg^{-1}.

The extraction efficiency, η can be calculated from the following mass balance

$$V_w c_{w0} = V_h c_h + \alpha V_w c_h \tag{7}$$

Assuming that headspace and water phase are in equilibrium, the ratio of the H_2 concentration in water and in the headspace is given by the Ostwald coefficient

$$\alpha = \frac{c_w}{c_h} \tag{8}$$

This gives for the initial concentration in the water

$$c_{w0} = \left(\frac{V_h}{V_w} + \alpha\right) c_h \tag{9}$$

and for the extraction efficiency as defined in equation (2)

$$\eta = \left(1 + \alpha \frac{V_w}{V_h}\right)^{-1} \tag{10}$$

In the present case, $\alpha = \alpha(H_2)$ was equal to 0.0163±0.0001, which gives η = 92 % for V_w/V_h = 8.4/1.6 = 5.25.

p_h was not measured and had to be estimated from the gas concentrations in the water.

$$\begin{aligned} p_h &= p_h(N_2) + p_h(O_2) + p_h(Ar) + p_h(CO_2) + p_h(H_2O) \\ &= RT\left[c_h(N_2) + c_h(O_2) + c_h(Ar) + c_h(CO_2)\right] + p_h(H_2O) \\ &= RT\left[\frac{c_{w0}(N_2)}{\frac{V_h}{V_w} + \alpha(N_2)} + \frac{c_{w0}(O_2)}{\frac{V_h}{V_w} + \alpha(O_2)} + \frac{c_{w0}(Ar)}{\frac{V_h}{V_w} + \alpha(Ar)} + \frac{c_{w0}(CO_2)}{\alpha(CO_2)}\right] + p_h(H_2O) \end{aligned} \tag{11}$$

The extraction efficiencies of all gases were assumed to follow their solubilities. Due to the buffering effect of the CO_2 system (CO_2(w), H_2CO_3, HCO_3^- and CO_3^{2-}), the dissolved CO_2 concentration changes by only 1 or 2 % during extraction, so that the headspace concentration can be estimated from $c_{w0}(CO_2)/\alpha(CO_2)$.

p_h was estimated to vary between 98 and 111 hPa, with contributions of 46 to 52 hPa from N_2, 23 to 27 hPa from O_2, 1.1 to 1.3 hPa from Ar, 0.4 hPa from CO_2 and 17 to 40 hPa from H_2O.

Based on equation (4), the **isotope delta of the headspace gas** can be calculated as follows

$$\delta_h = \frac{\delta_{htm} y_{htm}\left(1 + \frac{V_t}{V_h}\right) p_{htm} - \delta_m y_m \left[\left(1 + \frac{V_t}{V_h}\right) p_{htm} - p_h\right]}{y_{htm}\left(1 + \frac{V_t}{V_h}\right) p_{htm} - y_m \left[\left(1 + \frac{V_t}{V_h}\right) p_{htm} - p_h\right]} \tag{12}$$

Two alternative scenarios were considered to derive the initial isotope delta of dissolved H_2, with scenario 1 assuming equilibrium isotopic fractionation between headspace and water, and scenario 2 assuming kinetic isotopic fractionation during extraction from Niskin bottle to glass vessel.

Scenario 1: Correction of δ_h for equilibrium isotopic fractionation between headspace and water

The equilibrium isotope fractionation between water and headspace is defined as

$$\varepsilon = \frac{1+\delta_w}{1+\delta_h} - 1 \tag{13}$$

The isotopic mass balance equation between headspace and water can then be described via

$$V_w c_{w0} \delta_{w0} = V_h c_h \delta_h + V_w c_w \delta_w \tag{14}$$

which gives for the isotope delta of the original dissolved gas:

$$\delta_{w0} = \frac{\varepsilon(1+\delta_h)}{1+\frac{V_h}{V_w}\frac{1}{\alpha}} + \delta_h \tag{15}$$

The equilibrium isotope fractionation between dissolved phase and gas phase is ε = (37±1) ‰ at 20 ºC (Knox et al., 1992). The temperature dependence of ε is unknown and was neglected here.

Scenario 2: Correction for kinetic isotopic fractionation between headspace and water

If kinetic isotope fractionation applies, then the isotopic composition of the residual gas in the water is

$$\delta_w = (1+\delta_{w0})\left(\frac{c_w}{c_{w0}}\right)^{\varepsilon_k} - 1 = (1+\delta_{w0})\left(1-\eta\right)^{\varepsilon_k} - 1 \tag{16}$$

Then, the isotope delta of the accumulated gas in the headspace is

$$\delta_h = (1+\delta_{w0})\frac{1-(1-\eta)^{1+\varepsilon_k}}{\eta} - 1 \tag{17}$$

which gives for the isotope delta of the original dissolved gas:

$$\delta_{w0} = \frac{(1+\delta_h)\eta}{1-(1-\eta)^{1+\varepsilon_k}} - 1 \tag{18}$$

The kinetic isotope fractionation during gas evasion is ε_k = (–18±2)‰ at 20 ºC (Knox et al., 1992). The temperature dependence of ε_k is unknown and was neglected here.

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